

RADICAL PATHWAYS OF COAL DISSOLUTION IN DONOR MEDIA DURING REACTIONS OF COALS AND SPECIFICALLY DEUTERATED TETRALIN*

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INTRODUCTION

Recent studies utilizing deuterium labelling to trace the pathways of hydrogen transport between donor solvent, coal, and model compounds in the laboratories of Professor Leon Stock (Univ. of Chicago), Drs. L. A. Heredy, R. P. Skowronski and J. J. Ratto (Rockwell International) and in our own laboratory promise to provide a detailed understanding of mechanistic pathways operating at the molecular level during coal dissolution in donor media. Deuterium scrambling in donor solvents constitutes a sensitive probe of the structural features of coal and mineral matter. In previous papers^{1,2} we presented detailed information concerning the time dependence of the structural distribution of deuterium transferred to a subbituminous coal at 427°C in tetralin-1,1-d₂. In a preliminary report³ of our recent studies of high temperature reactions of specific radicals in the tetralin and alkylindan systems we presented evidence that 2-tetralyl as well as 1-tetralyl radical is formed during the oxidation of tetralin to naphthalene. The evidence for the intermediacy of 2-tetralyl was the observation of scrambling of deuterium from the 1- to the 2-position of tetralin during reaction with coal. In this paper we present a study of the scrambling and depletion of deuterium in reactions of a bituminous and a subbituminous coal with tetralin-1,1-d₂. Radical and ionic pathways responsible for major differences in scrambling rates for the two coals are discussed.

EXPERIMENTAL

Materials

Two coals were used in this study: Illinois #6 (Monterey) bituminous coal (C, 76.8%, H, 4.8%, S, 3.2%, N, 1.61% dry maf basis, 4.8% ash) and Kaiparowitz subbituminous coal (C, 77.3%, H, 1.2%, S, 0.8%, N, 1.2% dry maf basis, 8.5% ash). The coals were ground to -300 U.S. mesh and dried at 80°C and 10⁻² Torr.

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Tetralin-1,1-d₂ was prepared as described previously² except that the byproduct dihydronaphthalene was removed by treatment of the mixture of tetralin-1,1-d₂ and dihydronaphthalene with sufficient Br₂ to consume dihydronaphthalene followed by distillation of the lower boiling tetralin.

Procedure for the Reactions of Coals and Tetralin-1,1-d₂

Coal (0.75g) and Tetralin (1.5g) were loaded in a 3 in x 3/8 in Swagelok-capped type 316 stainless steel tube. The tube was plunged in a molten lead bath maintained at a suitably higher temperature such that the bath would attain the desired temperature (427 ± 5°C) within approximately one minute. The tube was withdrawn after the desired reaction time, quenched in water, and worked up as follows: The contents of the tube were washed into a beaker with tetrahydrofuran (THF), ca. 75 ml. The THF solution and fines were centrifuged for several minutes. The THF solution was decanted and the fines washed and centrifuged two more times to remove soluble material. The THF solutions were combined and concentrated to ca. 2 ml and added to 250 ml of pentane above a 0.45 µm Millipore filter. The preasphaltenes and asphaltenes precipitated and were collected on the filter and washed with three portions of pentane. Small portions of the pentane solutions were saved for gc analysis to determine methylindane, tetralin, and naphthalene yields. The pentane solutions were concentrated to an oil in a small flask which was attached to a short path vacuum distillation apparatus and tetralin, naphthalene and methylindane et al. were removed at 150°C and 10⁻¹ Torr, leaving the light oils behind. The tetralin/naphthalene mixture was separated into its components by preparative gc or by preparative liquid chromatography.

Deuterium Analysis

Isolated tetralin and naphthalene were first examined by proton-decoupled ²H Fourier transform nuclear magnetic resonance (FTNMR) spectroscopy (12.211 MHz) using a Varian model FT-80 instrument. The tetralin samples were then spiked with toluene-d₈ and reexamined by ¹H FTNMR. The toluene methyl resonance lies conveniently resolved between the two aliphatic resonances of tetralin. The toluene-d₈/tetralin ratio as determined by gas chromatography (gc) was used in conjunction with the toluene-d₈/tetralin FTNMR integral ratios to calculate the total isotope level in the recovered tetralin. The recovered tetralin and naphthalene were also examined by gc/mass spectrometry to determine the distribution of labeled species.

RESULTS AND DISCUSSION

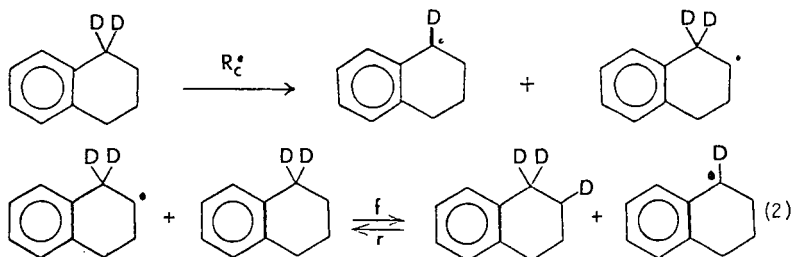
The distributions of deuterium label in the recovered tetralin and naphthalene are shown in Table 1. For Kaiparowitz coal, deuterium in the 1-position of tetralin decreases from 100% to 78% after 60 minutes' reaction. For Illinois No. 6, the deuterium content falls from 100% to 39% after 60 minutes, and the degree of scrambling is greater after only 5 minutes than the 60 minute reaction of Kaiparowitz. Incorporation of deuterium in the 2-position of tetralin to the extent of 11% occurs in 5 minutes with Illinois No. 6 but required 60 minutes with Kaiparowitz. A completely random distribution of deuterium would lead to 33% label in each of the aromatic 1- and

2-positions. The Kaiparowitz reaction was well short of complete scrambling at 60 minutes, but the Illinois No. 6 approaches complete scrambling at 35 minutes.

The exchange of deuterium between coal and tetralin occurs in both cases. Table 2 shows that about 25% of the label is lost from tetralin for either coal in 60 minutes. The rate of label loss appears slightly faster for Illinois No. 6 in the shorter reaction times. The total hydrogen uptake by the two coals, as measured by the conversion of tetralin to naphthalene, is identical for the two coals at 10 minutes' or less reaction time (Table 3). The Illinois No. 6 coal consumes slightly more hydrogen at long reaction times. This method is in error probably by about 3-5% of naphthalene yield since some tetralin becomes chemically bonded to fractions of the coal. It is further noted that the yields of 1-methylindan are only slightly greater at longer reaction times for Illinois No. 6.

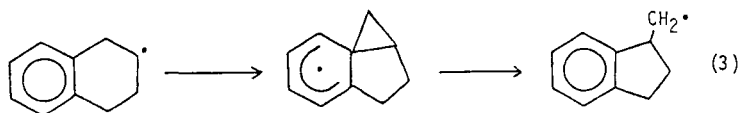
It is clear from these results that the degree of oxidation of tetralin at short reaction times is similar for the two coals and that both coals undergo label exchange with the coal, reminiscent of the results of Skowronski, Heredy and Ratto.⁴ The dramatic increase in scrambling rates induced by Illinois No. 6 coal at equal degrees of oxidation of the tetralin almost certainly indicates a different scrambling mechanism than that occurring with Kaiparowitz Coal.

In the conventional picture of coal dissolution, unimolecular cleavage of weaker C-C, C-S and C-O bonds in the coal leads to free radicals (eq. 1) which abstract hydrogen from the coal or donor solvent, or undergo disproportionation, combination, fragmentation and addition reactions, and participate in chain decompositions of hydrocarbons.



Ignoring the participation of phenolic or sulfur groups in the coal for the moment, the formation of 2-tetralyl and its subsequent reaction with the solvent (eq. 2) will lead to deuterium label in the 2-position. We have demonstrated⁵ in a study of high temperature reactions of tetralyl and indanylmethyl radicals that the 1-methylindan observed in the reactions of

coal and tetralin is a product of the reverse 1,2-aryl migration of 2-tetralyl radical (eq. 3).



This reaction is endothermic with an activation barrier of 22 ± 2 kcal/mole.⁵ The presence of 1-methylindan in coal reactions indicates that coal derived radicals are sufficiently non-selective to produce 2- as well as 1-tetralyl radicals.³ A second pathway of scrambling is the reverse of eq. 2. Reaction (2f) proceeds with $\Delta G = 0.1$ kcal/mole and $\Delta H = -16.1$ kcal/mole at 427°C , from thermochemical estimates of thermodynamic properties of 1- and 2-tetralyl radicals. Thus, although the reaction is slow, equal concentrations of 1- and 2-tetralyl radical would exist at equilibrium at 427°C . The direct unimolecular interconversion of 1-tetralyl and 2-tetralyl radicals is predicted not to occur due to the net antibonding configuration of the 1,2-hydrogen atom shift intermediate.⁷ Of course, 1,2-hydrogen shifts and alkyl shifts in carbonium ions proceed through a net bonding intermediate and occur very rapidly.

Thus, constituents of the coal which could convert radicals (which undergo relatively inefficient bimolecular interconversion) to carbonium ions (which undergo very rapid unimolecular rearrangements), would cause significant enhancements in scrambling rates. A likely candidate for the conversion of radicals to carbonium ions is the pyrite in Illinois No. 6 coal. Illinois No. 6 contains about 3% sulfur, two-thirds of which is associated with iron. By contrast, the low-sulfur Kaiparowitz contains only 40 ppm of iron. Reaction of Fe^{3+} with solvent radicals may lead to the corresponding carbonium ions



which would rapidly equilibrate the 1- and 2-hydrogens of tetralin. Consistent with this view, Bockrath has observed an enhanced rate of isomerization of tetralin to 1-methylindan with added pyrite. Whitehurst, et al, have observed that pyrite catalyzes solvent isomerization, dehydrogenation, and hydrogen transfer, though pyrite is by no means the only active catalytic agent.¹⁰ The form of iron is not specified in eq. 4. The oxidation of radicals by Fe^{3+} in aqueous media is well known.¹¹ However, more work is needed to identify the structure and mechanisms of the iron sulfide participation in

nonpolar donor media. Further work is underway in this laboratory to identify the structural features of coals which enhance hydrogen shuttling.

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TABLE 1.

DEUTERIUM LABEL DISTRIBUTIONS IN RECOVERED TETRALIN AND NAPHTHALENE

Coal	Reaction Time	Tetralin ^a		Naphthalene ^b	
		Arom	1 2	1 2	
Illinois No. 6	0	0	100	0	-- --
	2.5	5.6	91.8	2.5	91.3 8.7
	5.0	30.0	55.2	0.8	78.3 21.7
	10.0	29.9	51.7	18.4	74.6 25.4
	35.0	35.7	39.3	25.0	54.8 45.2
	60.0	36.6	38.8	24.6	59.1 40.8
Kaiparowitz	0	0	100	0	-- --
	10	2.5	95.4	2.1	45.1 4.9
	35	4.2	90.2	5.6	92.0 8.0
	60	10.9	78.2	10.9	87.5 12.5

^a % of deuterium in the aromatic, 1-, or 2-position^b % of deuterium in the 1- or 2-position

TABLE 2

ISOTOPE DEPLETION IN RECOVERED TETRALIN

Coal	Reaction Time, min	Deuterium Atoms/Molecule ^a
Illinois No. 6	0	2.0
	2.5	1.88
	5.0	1.64
	10.0	1.22 ^b
	35.0	1.68
	60.0	1.45
Kaiparowitz	0	2.0
	10	1.82
	35	1.56
	60	1.52

^a \pm 0.2 Atoms/molecule

^b This point is suspect due to a possible temperature error during the reaction.

TABLE 3

RECOVERED YIELDS OF TETRALIN, 1-METHYLINDAN AND NAPHTHALENE
AND HYDROGEN UPTAKE PER CARBON IN COAL^a

Coal	Reaction Time, min	Tetralin	1-methyl- indan	Naph- thalene	H uptake, Atoms/ Carbon Atom of Coal ^b
Illinois No.6	2.5	89.7	0.2	10.1	0.12
	5.0	86.3	0.3	13.4	0.17
	35	63.0	2.4	34.6	0.43
	60	51.9	3.5	44.6	0.55
Kaiparowitz	2.5	90.6	0.2	9.2	0.12
	5.0	86.1	0.3	13.5	0.17
	10	79.9	0.2	19.9	0.26
	25	72.7	1.9	26.8	0.34
	60	62.5	2.9	34.6	0.44

^a Yields of tetralin, 1-methylindan and naphthalene are normalized to 100%

^b Uses the yield of naphthalene recovered to estimate hydrogen uptake, neglects naphthalene and tetralin bound to coal products (~ 3%).